

## Lithium-ion Transfer at the Interface between Solid and Liquid Electrolytes under Applying DC Voltage

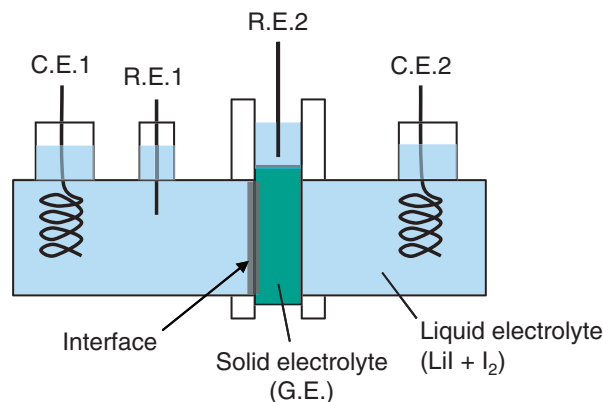
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We focused on the  $\text{Li}^+$  transfer at an interface between solid and liquid electrolytes by using asymmetric electrochemical impedance measurements to clarify the solvation and desolvation processes of  $\text{Li}^+$  ions. When DC voltage was imposed on the interface, the current-direction dependency of interfacial  $\text{Li}^+$ -transfer resistances was observed. Consequently, we would conclude that the desolvation process of  $\text{Li}^+$  transfer from liquid to solid electrolytes mainly governed the interfacial  $\text{Li}^+$  transfer.

Ion-transfer processes between heterointerfaces are essential for various functional devices such as Li-ion batteries (LIBs), solid oxide fuel cells, electrochemical sensors, etc. For LIBs, the  $\text{Li}^+$ -transfer process at the interface between electrode and electrolyte plays an important role for the cell performance. LIBs have been used as the power source of portable devices such as laptop computers and cellular phones. Moreover, LIBs are also expected to be the power sources for hybrid-electric and electric vehicles. These applications demand that LIBs meet strict requirements such as high power densities (fast charge and discharge reactions), longer cycle lives, etc. Recently, our group has reported that large activation energies were found through the interfacial  $\text{Li}^+$  transfer at heterointerfaces such as an electrode/electrolyte interface.<sup>1–3</sup> Through the electrochemical impedance analysis, however, we could not clearly distinguish between solvation and desolvation processes, since interfacial  $\text{Li}^+$ -transfer resistances include these two processes at the equilibrium conditions. Hence, it is required to clarify whether solvation or desolvation processes influence the activation energy of interfacial  $\text{Li}^+$  transfer. We focused on the applied DC voltage on the solid/liquid interface, since the  $\text{Li}^+$ -transfer resistance must be dependent on the direction of DC current.<sup>4,5</sup> In this letter, we measured interfacial  $\text{Li}^+$ -transfer resistances under various DC voltages by using an asymmetric four-probe cell.

An asymmetric Pt-four-probe electrochemical cell is shown in Figure 1. A  $\text{Li}^+$ -conducting solid electrolyte ( $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ , commercially available from OHARA Inc., abbreviated as G.E.) was sandwiched between nonaqueous liquid electrolytes of dimethyl sulfoxide (DMSO) or propylene carbonate (PC) solutions containing  $0.1 \text{ mol dm}^{-3}$   $\text{LiI}$  (anhydrous, 99.99% Aldrich) and  $1 \text{ mol dm}^{-3}$   $\text{I}_2$  (Nacalai tesque). One reference electrode (R.E.1) was immersed in one compartment together with one counter electrode (C.E.1), and the other reference electrode (R.E.2) was immersed in another compartment solely. DC voltages were applied from R.E.1 to R.E.2. While applying DC voltages at 0 (open circuit voltage, OCV),  $\pm 50$ , and  $\pm 100$  mV, electrochemical impedance measurements were conducted at an amplitude of 20 mV in a frequency region from 0.1 Hz–100 kHz. Potential sweep measurements were performed

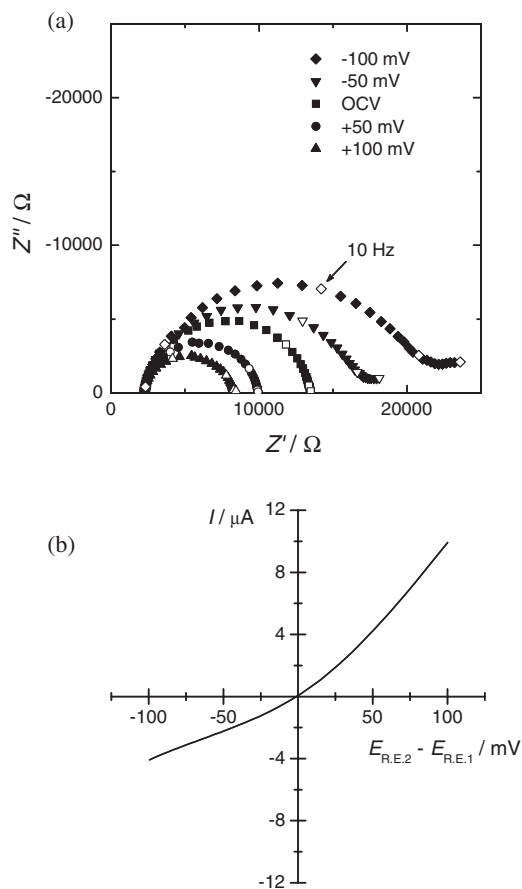


**Figure 1.** Schematic diagram of an asymmetric cell.

by applying DC voltages from  $-100$  to  $+100$  mV at a sweep rate of  $5 \text{ mV s}^{-1}$ .

Figure 2 shows the results of electrochemical impedance measurements and DC voltage polarization in the system of Pt/ $\text{LiI}+\text{I}_2$ -DMSO/G.E./ $\text{LiI}+\text{I}_2$ -DMSO/Pt. In the complex impedance plots, semicircles with the characteristic frequency around 10 Hz appeared. In this system, the four impedances due to the ion transfer should appear; 1) and 2)  $\text{Li}^+$ -transport resistances in the solid and the liquid electrolytes, 3) the  $\text{I}_2/\text{I}_3^-$  redox impedance at the interface of Pt/liquid electrolyte, and 4)  $\text{Li}^+$ -transfer resistance at the interface of solid/liquid electrolytes. To clarify the resistances of the first two components, the impedance spectra were obtained by the fabrication of two cells of Au/G.E./Au and Pt/ $\text{LiI}+\text{I}_2$ -liquid electrolyte/Pt. As a result, the transport was so sufficiently fast that no semicircles but only spikes appeared in the present frequency region. The  $\text{I}_2/\text{I}_3^-$  redox impedance does not appear because of the four-electrode measurements in which the redox reaction of  $\text{I}_2/\text{I}_3^-$  occurred on the counter electrodes. Thus, the semicircles around 10 Hz were attributed to interfacial  $\text{Li}^+$ -transfer resistance between solid and liquid electrolytes. In addition, the radii of these semicircles was changed by the DC voltages in the order of  $-100 \text{ mV} > -50 \text{ mV} > \text{OCV} > +50 \text{ mV} > +100 \text{ mV}$ . It should be noted that negative voltages caused the increase of interfacial  $\text{Li}^+$ -transfer resistances, while the positive voltages decreased the resistances. DC voltage polarization curve (Figure 2b) also shows the similar behaviors: The slope of current vs. applied voltage was steeper in the positive voltage region than in the negative those.

In the asymmetric electrochemical cell, DC voltage only influenced the interface depicted in Figure 1, thus we could focus on  $\text{Li}^+$  transfer through the interface. Therefore, by the applied positive DC voltages, the  $\text{Li}^+$ -transfer resistances from

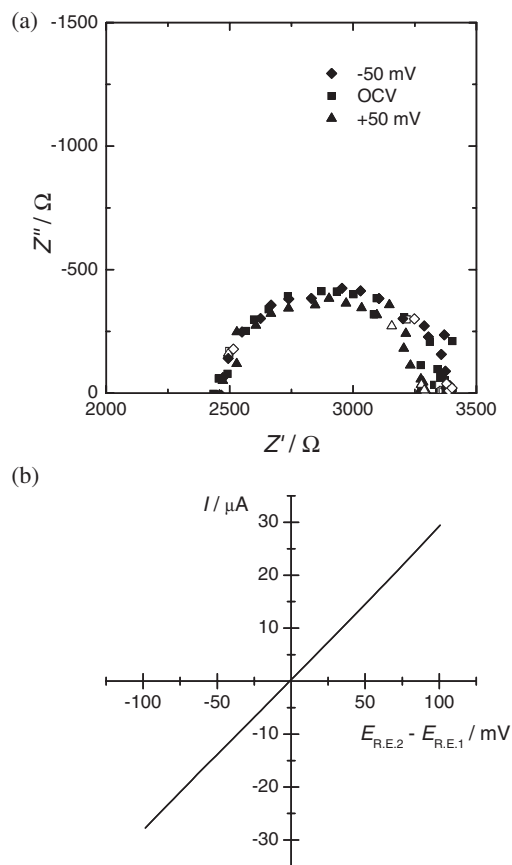


**Figure 2.** (a) Electrochemical impedance plots of Pt/LiI+I<sub>2</sub>-DMSO/G.E./LiI+I<sub>2</sub>-DMSO/Pt (30 °C) and (b) interface polarization between G.E. and LiI+I<sub>2</sub>-DMSO (rt, scan speed: 5 mV s<sup>-1</sup>).

solid to liquid electrolytes became explicit, and negative DC voltages gave the resistances from liquid to solid electrolytes. Generally, at a heterointerface, interfacial ion transfer from solid to liquid electrolytes is mainly determined by solvation process, and ion transfer from liquid to solid electrolytes by desolvation process. Thus larger interfacial Li<sup>+</sup>-transfer resistances in positive voltages indicates that a larger resistance existed in the desolvation process than in the solvation process in the present DMSO-based electrolytes.

In contrast, when we used PC-based electrolyte, the complex impedance plots and DC voltage polarization curves did not show the clear applied-voltage dependency (Figure 3) as compared with the case of DMSO-based electrolyte. These differences in the voltage dependency between PC and DMSO systems can be explained by the donor numbers of PC and DMSO. Since donor numbers are 15.1 and 29.8 for PC and DMSO,<sup>6</sup> respectively; therefore, DMSO can solvate Li<sup>+</sup> ions more strongly.<sup>7</sup> Therefore, obvious current-direction dependency could be found in DMSO solutions but not in PC solutions.

In conclusion, we shed light on interfacial Li<sup>+</sup> transfer by using an asymmetric cell and found that the desolvation process predominantly determined the interfacial Li<sup>+</sup> transfer across liquid/solid electrolytes. And, it is shown that applying DC



**Figure 3.** (a) Electrochemical impedance plots of Pt/LiI+I<sub>2</sub>-PC/G.E./LiI+I<sub>2</sub>-PC/Pt (30 °C) and (b) interface polarization between G.E. and LiI+I<sub>2</sub>-PC (rt, scan speed: 5 mV s<sup>-1</sup>).

voltages in an asymmetric cell is a powerful tool for the investigation of the interfacial ion-transfer phenomena involved in heterointerfaces.

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